

## AMBIENT TEMPERATURE CURING COATING COMPOSITION

5 <sup>5/27</sup> The present invention claims priority of European Patent Application Serial No. 000305345.1, filed on June 23, 2000.

Background of the Invention

10 The present invention relates to a coating composition that is fast curing at ambient temperature (touch dry in less than 2 hours at 25°C) with a high solids content (> 70 % by weight) and a low VOC (< 250 grams solvent per litre of the composition, g/l) which can be used in durable protective coatings.

15 There has been increased concern in recent years about the release of volatile solvents into the atmosphere, and there has been a consequent need to reduce the volatile organic solvent content of coating, sealant, and adhesive compositions. This has not been easy for coating compositions, which require a relatively low viscosity of below 20 Poise for application by the usual methods of spray, roller or brush, and particularly not for coating compositions which have to be applied and cure rapidly at ambient temperature, for example coatings for large structures such as ships, bridges, buildings, industrial plants, and oil rigs.

20 Coating compositions generally need to contain a polymer to confer film-forming properties, but any polymer used needs to be of sufficient molecular weight to give the required low viscosity, particularly after pigmentation as a paint. Such low-viscosity polymers often require long curing times to develop satisfactory mechanical properties, especially when cured at low temperature.

25 In WO 98/04594 a process is disclosed for the preparation of a curable polymer composition by polymerisation of a functional olefinically unsaturated monomer in the presence of a reactive diluent which is a liquid organic compound of viscosity less than 2 Pa.s (20 Poise) having at least one functional group which is substantially non-reactive with the functional olefinically unsaturated monomer and which is capable of reacting with a curing agent to form a

polymer network. The major drawback of this technology is that this low-viscous coating material results in a low final film  $T_g$  and moderate durability.

In WO 96/16109 and WO 98/32792 an epoxy-polysiloxane coating composition  
5 is disclosed that is prepared by combining water, a polysiloxane, a difunctional aminosilane hardener, optionally an organooxysilane, and a non-aromatic epoxy resin. The maximum amount of solvent added to these compositions is approximately 420 g/l. The compositions are intended to be used as protective coatings for primed or galvanised steel, aluminium, concrete, and other  
10 substrates at a dry film thickness in the range of 25  $\mu\text{m}$  to about two millimetres. Whilst these compositions are employed as durable topcoats, their gloss and colour retention properties when exposed to natural or accelerated test conditions (UV-A, UV-B) are not as expected for polysiloxane based compositions. This strongly affects the appearance of a coated substrate.

15 US 4,446,259 discloses a coating composition having a liquid carrier and a binder which is a blend of an olefinically unsaturated polymer containing glycidyl groups and a crosslinkable polysiloxane having attached to the silicone atoms of its backbone alkyl, phenyl, and hydroxyl groups. These compositions  
20 are used as ambient temperature curing protective coatings. The major drawback of these compositions is the presence of a relatively large amount of organic solvent in the composition.

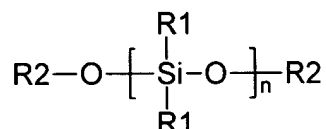
EP 0 822 240 discloses a coating resin composition comprising a silica-  
25 dispersed oligomer solution of an organosilane, an acrylic resin, and a curing catalyst. The coating resin compositions on average have a solid content in the range of 40 - 50% by weight. Consequently, these coating compositions have a VOC well above 250 g/l.

30 The present invention provides a solution to the drawbacks associated with the above-mentioned prior art.

Summary of the Invention

In one embodiment, the ambient temperature curing coating composition according to the present invention comprises:

5



- a linear or branched polysiloxane having the formula

wherein each R1 is independently selected from the group consisting of alkyl, aryl, alkoxy groups having up to six carbon atoms, reactive glycidoxy groups, and OSi(OR3)<sub>3</sub> groups, wherein each R3 independently has the same meaning as R1, each R2 is selected from the group consisting of hydrogen and alkyl and aryl groups having up to six carbon atoms, and wherein n is selected so that the number average molecular weight of the polysiloxanes is in the range of from 200 to about 5,000, preferably 500 – 2,000, and

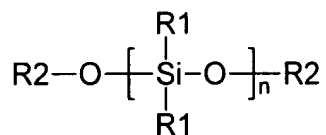
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- an alkoxysilyl-functional acrylic polymer,

wherein said coating composition is curable with a curing agent consisting essentially of atmospheric moisture and/or water. Thus, in this embodiment, the coating composition is effectively cured with the curing agent defined above; that is, the coating composition is substantially free of any other curing agent.

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In another embodiment, the invention relates to an ambient temperature curing coating composition comprising



- a polysiloxane having the formula

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wherein each R1 is selected from the group consisting of alkyl, aryl, and

alkoxy groups having up to six carbon atoms, reactive glycidoxo groups, and  $\text{OSi}(\text{OR}_3)_3$  groups, wherein each  $\text{R}_3$  independently has the same meaning as  $\text{R}_1$ , each  $\text{R}_2$  is selected from the group consisting of hydrogen and alkyl and aryl groups having up to six carbon atoms, and wherein  $n$  is selected so that the molecular weight of the polysiloxanes is in the range of from 500 to about 2,000, and

- an alkoxysilyl-functional acrylic polymer
- an amino-functional compound,

wherein the amino-functional compound is an aminosilane of general formula  $\text{Y-Si}(\text{O-X})_3$ , wherein  $\text{Y}$  is  $\text{H}(\text{HNR})_a$  and  $a$  is an integer from one to six, each  $\text{R}$  is a difunctional organic radical independently selected from the group consisting of aryl, alkyl, dialkylaryl, alkoxyalkyl, and cycloalkyl radicals, and  $\text{R}$  can vary within each  $\text{Y}$  molecule, each  $\text{X}$  may be the same or different, and is limited to alkyl, hydroxyalkyl, alkoxyalkyl, and hydroxyalkoxyalkyl groups containing fewer than about six carbon atoms.

#### Detailed Description of the Invention

For the purpose of the present invention an alkoxysilyl-functional acrylic polymer is a polymer prepared by copolymerising at least three different olefinically unsaturated monomers whereby at least one of the monomers is an alkoxysilyl-functional olefinically unsaturated monomer.

It is preferred that  $\text{R}_1$  and  $\text{R}_2$  comprise groups having fewer than six carbon atoms to facilitate rapid hydrolysis of the polysiloxane, which reaction is driven by the volatility of the alcohol analogue product of the hydrolysis.  $\text{R}_1$  and  $\text{R}_2$  groups having more than six carbon atoms tend to retard or slow the crosslinking of the polysiloxane due to the relatively low volatility of each alcohol analogue. Preference is given to the use of alkoxysilyl-functional polysiloxane. Methoxy-, ethoxy-, and silanol-functional polysiloxanes having number average molecular weights in the range of about 400 to about 2000 are preferred for formulating coating compositions according to present invention. Methoxy-, ethoxy-, and silanol-functional polysiloxanes having molecular weights of less

than 400 would produce a coating composition that would be brittle and offer poor impact resistance. Any liquid methoxy-, ethoxy-, and silanol-functional polysiloxane with a molecular weight above 400 can be used, though it is preferred to use polysiloxanes with a molecular weight of less than 2000, as they enable the production of compositions that require few if any additional solvents to achieve application viscosity, i.e. which can be used without adding solvent in excess of current volatile organic content (VOC) requirements. Small amounts of methoxy-, ethoxy-, and silanol-functional polysiloxanes having molecular weights of less than 400 (<10% mass of the coating) can be tolerated to help reduce viscosity without adversely affecting the physical properties of the resultant films. In general, a high-molecular weight polysiloxane can be used without violating VOC requirements by mixing it with a reactive or non-reactive diluent. However, normally this will affect film properties.

Suitable polysiloxanes that can be used in the composition according to the present invention include: DC 3037 and DC 3074 (both ex Dow Corning), or SY 231, SY 550, and MSE 100 (all ex Wacker).

The alkoxysilyl-functional acrylic polymer is prepared by copolymerising at least three different olefinically unsaturated monomers whereby at least one of the monomers is an alkoxysilyl-functional olefinically unsaturated monomer. This process is another aspect of the present invention.

Examples of ethylenically unsaturated monomers which can be copolymerised with such an alkoxysilyl-functional olefinically unsaturated monomer are acrylic esters such as butyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-hexyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl methacrylate or acrylate, cyclohexyl (meth)acrylate, 2,2,5-trimethylcyclohexyl (meth)acrylate, isobornyl (meth)acrylate, acrylonitrile, methacrylonitrile, trimethoxysilyl propyl(meth)acrylate, and vinyl compounds such as styrene, vinyl acetate or vinyl chloride, wherein the notation (meth)acrylate means acrylate or methacrylate.

The alkoxysilyl-functional olefinically unsaturated monomer in general can be any one of the above-mentioned olefinically unsaturated monomers functionalised with one or more alkoxysilyl groups. Trimethoxysilylpropyl

methacrylate is one of the preferred monomers in the preparation of the alkoxyethyl-functional acrylic polymer.

To prepare a coating composition with a low VOC, the alkoxyethyl-functional acrylic polymer can be prepared, for example, by free radical polymerisation or  
5 any other reaction in the presence of a reactive diluent which is an organic compound of viscosity less than 2 Pa.s (20 Poise) at 25°C. Preference is given to the use of a reactive diluent having at least one functional group which is substantially non-reactive with the olefinically unsaturated monomers and which  
10 is capable of reacting with a curing agent to form a polymer network. It was found that low-viscosity polysiloxanes can be used in the preparation of the alkoxyethyl-functional acrylic polymer that is present in the coating composition according to the present invention.

In a highly preferred embodiment, the reactive diluent is a polysiloxane, and this  
15 polysiloxane is the same as the polysiloxane that is present in the coating composition according to the present invention.

Reactive diluents that can be used in the preparation of the alkoxyethyl-functional acrylic polymer include alkoxyethyl-functional polysiloxanes, such as  
20 DC 3037 and DC 3074 (both ex Dow Corning), or SY 231, SY 550, and MSE 100 (all ex Wacker), monomeric alkoxyethylsilanes, such as tetraethylorthosilicate, trimethoxypropyl silane and dimethoxydiphenyl silane, and organofunctional monomeric alkoxyethylsilanes, such as glycidoxypropyl trimethoxyethylsilane, glycidoxypropyl triethoxyethylsilane, acetoacetoxypropyl trimethoxyethylsilane, and  
25 acetoacetoxypropyl triethoxyethylsilane.

Alkoxy groups attached to silicon are curable by moisture, so preferably care should be taken to exclude moisture during the polymerisation and subsequent storage of the polymer.

30 Very good results are achieved when the alkoxyethyl-functional acrylic polymer is obtained by polymerising a mixture comprising trimethoxyethylpropyl methacrylate, methylmethacrylate and butyl acrylate in the polysiloxane that is

also present in the coating composition. Optionally, the mixture further comprises other acrylic monomers, e.g. butyl methacrylate. In general, it can be said that good results are achieved when the mixture comprises 30 - 80 % by weight of polysiloxane, 2 -25% by weight of trimethoxysilylpropyl methacrylate, 1 - 40% by weight of methyl methacrylate, and 1 - 40% by weight of butyl acrylate. Better results are achieved when the mixture comprises 40-70 % by weight of polysiloxane, 4-15% by weight of trimethoxysilylpropyl methacrylate, 10-30% by weight of methyl methacrylate, and 10-30% by weight of butyl acrylate, wherein the % by weight is calculated based on the total amount of all components present in the mixture before the start of the polymerisation reaction.

As indicated above, preference is given to a process for the preparation of the alkoxysilyl-functional acrylic polymer from ethylenically unsaturated monomer by addition polymerisation while in solution. The polymerisation is preferably carried out in the substantial absence of non-functional volatile solvent, that is, a solvent that will not react with the curing agent for the polymer.

Alternatively, a small proportion, for example up to 10 to 20% by weight of the polymerisation reaction mixture, of a non-functional volatile solvent which is miscible with the reactive diluent can be present. Some or all of the monomers can be pre-dissolved in the reactive diluent, but preferably the monomers, together with (a) free radical initiator(s) and any chain transfer agent used, are gradually added to the diluent. For example, the reactive diluent can be heated to a temperature in the range of 50 - 200°C, and the monomers, initiator, and chain transfer agent are added over a period of up to 12 hours, preferably in 4 hours, while the temperature of the solution is maintained during the addition and for a further period of 0.5 - 4 hours after the addition. A further charge of initiator may be added during this further period to reduce the level of unreacted monomer. However, it is also possible to reduce this level by distilling off the unreacted monomer from the reaction mixture.

The free radical initiator can for example be a peroxide or peroxy-ester such as benzoyl peroxide, di-tert-butyl peroxide, tert-butyl peroxy-3,5,5-

trimethylhexanoate, 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane, or tertiary butyl peroctoate or an azo compound such as azobisisobutyronitrile or azo-bis(2-methylbutyronitrile).

- 5 A chain transfer agent, for example dodecanethiol, butanethiol, pentaerythritol tetra (mercaptopropionate), mercaptopropyl trimethoxysilane, or dibutyl phosphite, may be present during polymerisation. The level of initiator and of chain transfer agent, if present, is preferably controlled so that the number average molecular weight  $M_n$  of the polymer produced is not more than 20,000  
10 and is preferably in the range of 600 to 5,000, most preferably 1,000 to 3,000, in order to maintain a workable viscosity. However, it is possible to get a workable composition using a polymer with a molecular weight above 20,000 albeit that relatively high levels of monomeric compounds and/or solvent need to be added to achieve application viscosity. For example, the amount of free  
15 radical initiator used (by weight based on monomers) is generally at least 0.5%, preferably 1 to 10%, when no chain transfer agent is used, or a level of 0.5 to 5% initiator can be used in conjunction with 1 to 10% chain transfer agent.

In a preferred embodiment, 100 parts by weight of the coating composition comprise 50 - 70 parts by weight of a polymer composition comprising from 45  
20 to 75% by weight of the polysiloxane and from 20 to 45% by weight of the alkoxysilyl-functional acrylic polymer. Optimum results are found for a polymer composition comprising from 50 to 70% by weight of the polysiloxane and from 20 to 40% by weight of the alkoxysilyl-functional acrylic polymer. The % by weight is calculated on the basis of the weight of the polymer composition.

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The coating composition according to the present invention optionally also comprises a curing catalyst. The curing catalyst in general can be any curing catalyst active in crosslinking the alkoxysilyl-functional groups present in the acrylic polymer and/or in the reactive diluent under the intended conditions of  
30 curing. Examples of general classes of catalysts that can be used include basic catalysts (amines or inorganic bases), acidic catalysts (organic and inorganic acids, both Lewis and Brønsted acids), and mixtures thereof.



The curing catalyst can for example be amino-functional. Preferably, the curing agent is an amine chosen from the general classes of aliphatic amines, aliphatic amine adducts, polyamidoamines, cycloaliphatic amines and cycloaliphatic amine adducts, aromatic amines, Mannich bases, and ketimines, which each may be substituted wholly or in part with an aminosilane having the general formula  $Y-Si-(O-X)_3$ , wherein Y is  $H(HNR)_a$  and a is an integer from one to six, each R is a difunctional organic radical independently selected from the group consisting of aryl, alkyl, dialkylaryl, alkoxyalkyl, and cycloalkyl radicals, and R can vary within each Y molecule. Each X may be the same or different, and is limited to alkyl, hydroxyalkyl, alkoxyalkyl, and hydroxyalkoxyalkyl groups containing fewer than about six carbon atoms.

Preferred aminosilanes are, for example: 3-aminoethyl triethoxysilane, 3-aminopropyl triethoxysilane, n-phenylaminopropyl trimethoxysilane, trimethoxysilylpropyl diethylene triamine, 3-(3-aminophenoxy)propyl trimethoxysilane, aminoethyl aminomethylphenyl trimethoxysilane, 2-aminoethyl 3-aminopropyl, tris 2-ethylhexoxysilane, n-aminoethyl aminopropyl trimethoxysilane, and trisaminopropyl trimethoxy ethoxysilane, or mixtures thereof. However, the curing agent can also contain a polyamine.

It was found that the addition of up to 20 % by weight of aminosilanes to the coating composition according to the present invention not only improves the physical properties of the cured coating such as hardness and gloss retention, but also improves the adhesion of the coating to the substrate.

The coating compositions according to the invention may contain additional compounds that act as a catalyst for Si-O-Si condensation. In general, the coatings are capable of curing under ambient temperature and humidity conditions to a tack-free coating in 2 to 20 hours even without such a catalyst, but a catalyst may be preferred to give a faster cure.

One example of a catalyst for Si-O-Si condensation is an alkoxytitanium compound, for example a titanium chelate compound such as a titanium bis(acetylacetonate) dialkoxide, e.g., titanium bis(acetylacetonate)

diisopropoxide, a titanium bis(acetoacetate) dialkoxide, e.g., titanium bis(ethylacetoacetate) diisopropoxide, or an alkanolamine titanate, e.g., titanium bis(triethanolamine) diisopropoxide, or an alkoxytitanium compound which is not a chelate such as tetra(isopropyl) titanate or tetrabutyl titanate. Such titanium compounds containing alkoxy groups bonded to the titanium may not act as catalysts alone, since the titanium alkoxide group is hydrolysable and the catalyst may become bound to the cured silane or siloxane by Si-O-Ti linkages. The presence of such titanium moieties in the cured product may be advantageous in giving even higher heat stability. The titanium compound can for example be used at 0.1 to 5% by weight of the binder. Corresponding alkoxide compounds of zirconium or aluminium are also useful as catalysts.

An alternative catalyst is a nitrate of a polyvalent metal ion such as calcium nitrate, magnesium nitrate, aluminium nitrate, zinc nitrate, or strontium nitrate. Calcium nitrate has been suggested as a catalyst for the amine curing of epoxy resins, but it has never been suggested for the curing of silane or siloxane materials. Surprisingly, we have found that calcium nitrate is an effective catalyst for the curing by Si-O-Si condensation of a silane or siloxane containing at least two alkoxy groups bonded to silicon by Si-O-C bonds, when the composition also includes an organic amine. The calcium nitrate is preferably used in its tetrahydrate form but other hydrated forms can be used. The level of calcium nitrate catalyst required is generally not more than 3% by weight of the binder, for example 0.05 to 3% by weight. Coatings cured using calcium nitrate catalyst are especially resistant to yellowing on exposure to sunlight.

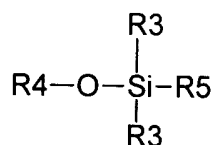
Another example of a suitable catalyst is an organotin compound, for example a dialkyltin dicarboxylate such as dibutyltin dilaurate or dibutyltin diacetate. Such an organotin catalyst can for example be used at 0.05 to 3% by weight of the binder of the coating composition.

Other compounds effective as catalysts in the coating compositions of the invention are organic salts, such as carboxylates of bismuth, for example

bismuth tris(neodecanoate). Organic salts and/or chelates of other metals such as zinc, aluminium, zirconium, tin, calcium, cobalt, or strontium, for example zirconium acetylacetonate, zinc acetate, zinc acetylacetonate, zinc octoate, stannous octoate, stannous oxalate, calcium acetylacetonate, calcium acetate, calcium 2-ethylhexanoate, cobalt naphthenate, calcium dodecylbenzenesulphonate, or aluminium acetate, may also be effective as catalysts.

It was found that in coating compositions comprising an glycidyl-functional monomeric alkoxysilane as a reactive diluent, in addition to one or more of the catalysts mentioned above, also mercapto-functional catalysts can be used. Further, in coating compositions comprising an aceto-functional monomeric alkoxysilane as a reactive diluent, in addition to one or more of the catalysts mentioned above, also (meth)acrylate-functional catalysts can be used.

Optionally, the coating composition according to the present invention comprises a low-molecular weight alkoxysilane having the general formula



wherein R3 is selected from the group consisting of alkoxy, alkyl and cycloalkyl groups containing up to six carbon atoms and aryl groups containing up to ten carbon atoms. R4 is independently selected from the group consisting of alkyl, hydroxyalkyl, alkoxyalkyl, and hydroxyalkoxyalkyl groups containing up to six carbon atoms. R5 is independently selected from the group consisting of alkyl, alkoxy, hydroxyalkyl, alkoxyalkyl, and hydroxyalkoxyalkyl groups containing up to six carbon atoms. An example of a low-molecular weight alkoxysilane according to the above formula that can be used in the coating composition is dimethoxydiphenyl silane.

The coating compositions of the invention may further comprise one or more

additional ingredients. They may, for example, comprise one or more pigments, for example titanium dioxide (white pigment), coloured pigments such as yellow or red iron oxide or a phthalocyanine pigment and/or one or more strengthening pigments such as micaceous iron oxide or crystalline silica and/or one or more  
5 anticorrosive pigments such as metallic zinc, zinc phosphate, wollastonite or a chromate, molybdate or phosphonate and/or a filler pigment such as barytes, talc or calcium carbonate. The composition may comprise a thickening agent such as fine-particle silica, bentonite clay, hydrogenated castor oil, or a polyamide wax. The composition may also comprise a plasticiser, pigment  
10 dispersant, stabiliser, flow aid, or thinning solvent.

The coating compositions of the invention generally cure at ambient temperatures, for example 5 to 30°C, and are thus suitable for application to large structures where heat-curing is impractical. The coating compositions of  
15 the invention alternatively can be cured at elevated temperatures, for example from 30 to 50°C up to 100 or 130°C, to speed up the curing. The hydrolysis of silicon-bonded alkoxy groups depends on the presence of moisture; in almost all climates atmospheric moisture is sufficient but a controlled amount of moisture may need to be added to the coating when curing at elevated  
20 temperature or when curing in very low humidity (desert) locations. The water is preferably packaged separate from any compound or polymer containing silicon-bonded alkoxy groups.

The coating compositions of the invention in general can be used as finish  
25 coatings and/or primer coatings. Coating compositions containing a relatively high proportion of polysiloxane have a high gloss which is retained remarkably well on weathering and UV exposure. They are particularly suitable for coating substrates which are exposed to the weather, e.g. sunlight, for long periods before recoating. The highest levels of gloss may be achieved if the coating  
30 composition includes an organic solvent (thinner) such as xylene, although use of solvent is not generally necessary in the coating compositions of the invention, which can be 100% solids coatings having a very low measured

volatile organic content. The coating composition may contain an alcohol, e.g. ethanol or butanol, preferably packaged with the alkoxysilyl-functional component. A finish coating according to the invention can be applied over various primer coatings, for example inorganic zinc silicate or organic zinc-rich silicate primers and organic, e.g. epoxy resin, primers containing zinc metal, corrosion-inhibiting, metal flake or barrier pigments. The coating composition of the invention has particularly good adhesion to inorganic zinc silicate coatings without needing an intermediate tie coat or mist coat. A finish coating composition of the invention can also be applied directly over aluminium or zinc "metal spray" coatings, in which case it acts as a sealer as well as a top coat, or over galvanised steel, stainless steel, aluminium, or plastics surfaces such as glass fibre reinforced polyester or a polyester gel coat. The coating composition can for example be used as a finish coating on buildings, steel structures, automobiles, aircraft and other vehicles, and general industrial machinery and fitments. The finish coating can be pigmented or it can be a clear (non-pigmented) coat, particularly on cars or yachts. For such applications the use of UV absorbers such as Cytec 1164 (ex Cytec) and hindered amine light stabilisers such as Tinuvin 292 (ex Ciba) are desirable. The coating composition can be applied directly to prepared carbon steel as a primer/finish.

Since the mixture of polysiloxane and the alkoxysilyl-functional acrylic polymer is curable by moisture, it is possible that these components, in the absence of any further agent that might initiate the curing reaction, are packed together as a so-called one-pack composition. Special care should be taken that the mixture is not contacted with any moisture before the coating is applied.

However, if a curing catalyst is present in the coating composition, the catalyst is normally packaged separately from the (pigmented) polymer. The components are mixed together shortly before application of the coating. Fast drying storage stable one-pack systems are possible using "duplex" tins where the catalyst is stored separate to the paint in one can.

The coating composition of the invention alternatively can be used as a

protective primer coating, particularly on steel surfaces, for example bridges, pipelines, industrial plants or buildings, oil and gas installations, or ships. For this use it is generally pigmented with anticorrosive pigments. It may for example be pigmented with zinc dust; coatings according to the invention  
5 have a similar anticorrosive performance to known zinc silicate coatings but are less liable to mud-cracking and can be readily overcoated, particularly with a polysiloxane finish, for example a finish coat according to the present invention. Primer coating compositions according to the invention can be used as maintenance and repair coatings on less than perfect surfaces such as  
10 aged blasted steel or "ginger" (steel which has been blasted and has started to rust in small spots), hand-prepared weathered steel, and aged coatings.

As well as outstanding resistance to UV weathering, the coatings produced from the compositions of the invention have good flexibility and adhesion to  
15 most surfaces and have higher heat resistance (up to 150°C and usually up to 200°C) than most organic coatings.

The invention will be elucidated with reference to the following examples. These are intended to illustrate the invention but are not to be construed as limiting in  
20 any manner the scope thereof.

In the examples, pbw has the meaning of parts by weight.

## Examples

### Example 1

<u>Formulation</u>	<u>Parts by weight</u>
Butyl Acetate	40.0
Silres SY231	100.0
Trimethoxysilyl propylmethacrylate	36.7
Butyl Acrylate	94.6
Methyl Methacrylate	59.1
t.butyl perethylhexanoate	9.6
Silres SY231	60.0

5

Silres SY231 (100.0g) and butyl acetate (40.0g) are charged to a vessel fitted with a condenser, a N<sub>2</sub> purge, a stirrer, a thermometer, and an addition port. The reagents are heated to 150<sup>0</sup>C under a N<sub>2</sub> atmosphere. The monomers and initiator (dissolved in Silres SY231) are charged separately to the heated reaction vessel over two hours and held at 150<sup>0</sup>C for a further hour. An initiator boost of 1g is added and the vessel is held at 150<sup>0</sup>C for a further hour. The resultant polymer has a viscosity of 11.1 poise (cone and plate viscometer at 25<sup>0</sup>C) with a non-volatile content of 86.1%.

10

### 15 Example 2

The polymer described in example 1 was used to prepare the following coating composition:

<u>Formulation</u>	<u>Parts by weight</u>
Polymer (example 1)	165.0
Titanium Dioxide	75.0
Triethylorthoformate	0.8
Bentone SD3	1.2
Dibutyl tin dilaurate	3.0
Solsperse 24000	1.5
Tinuvin 292	0.8

5 The polymer, solspers 24000, bentone and tinuvin 292 were mixed together under high shear. The titanium dioxide was added slowly under stirring and dispersed under high shear until the pigment had a particle size of less than 10 $\mu$  (as measured by Hegman gauge). The paint was allowed to cool and the triethyl orthoformate and dibutyl tin dilaurate were added under stirring. The resultant paint dried in less than 6 hours at ambient temperature.

10 This paint possessed excellent durability having a gloss retention of approximately 90% after 1500MJ EMMAQUA exposure, which is equivalent to 5 years exposure to Florida weather conditions.

#### Examples 3-11

15

<u>Example Number</u>	<u>Methyl Methacrylate</u>	<u>Butyl Acrylate</u>	<u>Trimethoxysilyl Methacrylate</u>	<u>Silres SY231</u>	<u>Triganox 21S</u>
3	17.2	27.2	15	39.6	1
4	10	40	5	43	2
5	10	24	15	50	1
6	25	39	5	30	1
7	22	40	5	30	3
8	11	40	15	31	3
9	25	27	15	30	3
10	25	27	5	40	3
11	17	15	15	50	3

The polymers, whose formulations are described above, were prepared as



described in example 1. The viscosities and non-volatile contents of the polymers are tabulated below.

<u>Example Number</u>	<u>Viscosity</u> (Poise)	<u>Non Volatile Content.</u> (g/l)
3	11.5	88.58
4	15.0	88.98
5	12.7	88.62
6	65.5	89.20
7	42.5	88.93
8	15.9	89.02
9	57.0	87.87
10	34.4	88.40
11	5.7	86.86

#### 5 Examples 12-20

The polymers prepared in examples 3-11 were used to prepare a series of coating compositions utilising the formulation described below.

<u>Formulation</u>	<u>Parts by weight</u>
Polymer (example 3-11)	220.0
Titanium Dioxide	100.0
Triethylorthoformate	1.0
Aminopropyltriethoxysilane	16.0
Xylene	32.0

- 10 The drying speeds (as determined by BK track recorder at laboratory ambient temperature and relative humidity) and paint viscosities (Cone and Plate Viscometer at 250C) are tabulated below.

<u>Example Number</u>	<u>Viscosity (Poise)</u>	<u>Drying Time</u> (Hours)
12	0.7	4:45
13	1.0	4:45
14	1.0	1:45
15	2.1	13:00
16	1.5	7:00
17	0.9	2:00
18	1.9	1:45
19	1.1	5:00
20	0.5	2:45

Examples 21-31

<u>Example Number</u>	<u>Methyl Methacrylate</u>	<u>Butyl Acrylate</u>	<u>Trimethoxysilyl Methacrylate</u>	<u>Silres SY231</u>	<u>Di-t-butyl peroxide</u>
21	272.5	30.0	117.5	80.0	11.4
22	300.0	37.5	50.0	112.5	10.0
23	250.0	50.0	100.0	100.0	12.5
24	222.5	30.0	155.0	92.5	13.9
25	300.0	37.5	50.0	112.5	10.0
26	300.0	25.0	125.0	50.0	10.0
27	300.0	50.0	100.0	50.0	10.0
28	300.0	25.0	87.5	87.5	10.0
29	222.5	30.0	92.5	155.0	13.9
30	300.0	50.0	100.0	50.0	10.0
31	200.00	25.00	200.0	75.0	15.0

- DC3074 a xylene (100g) was charged to a vessel fitted with condenser, N<sub>2</sub> purge, stirrer, thermometer and addition port. The DC3074 was heated to 140°C under a N<sub>2</sub> atmosphere. The monomers and initiator were charged, as a single feed, to the heated reaction vessel over two hours and held at 140°C for a further hour. An initiator boost of 0.3g was added and the vessel was held at 140°C for a further hour. The physical properties of the polymers are tabulated below.

<u>Example Number</u>	<u>Viscosity (Poise)</u>	<u>Non Volatile Content (g/l)</u>
21	5.2	81.88
22	8.4	82.17
23	10.4	82.34
24	12.2	82.61
25	8.0	81.93
26	2.3	82.08
27	2.4	81.51
28	4.2	81.90
29	47.8	81.84
30	2.3	82.07
31	9.5	82.24

Examples 32-42

- The polymers described in examples 21-31 were used to prepare a series of coating compositions utilising the formulation described below.

<u>Formulation</u>	<u>Parts by weight</u>
Polymer (example 21-31)	180.0
Titanium Dioxide	80.0
Aminopropyltriethoxysilane	10.0
Xylene	10.0

- The drying time (as determined by BK track recorder at laboratory ambient temperature and relative humidity), paint viscosities (Cone and Plate Viscometer at 25<sup>0</sup>C) and non-volatile content (mass loss after 7 days cure at laboratory ambient) are tabulated below.

<u>Example Number</u>	<u>Drying Time</u> (Hours)	<u>Viscosity</u> (Poise)	<u>Non Volatile Content</u> (g/l)
32	3:00	4.79	219.6
33	1:50	8.15	203.5
34	1:15	11.12	203.1
35	3:00	8.75	201.3
36	2:00	3.68	213.9
37	6:00	1.43	232.9
38	2:15	1.47	241.2
39	4:30	1.97	171.9
40	2:15	16.9	216.5
41	2:15	2.48	231.5
42	1:15	27.98	220.5

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